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The Temperature Dependence of the Surface Tension of Water

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Abstract. IAPS issued a release on the temperature dependence of surface tension of an ordinary water substance in 1976. The equation for the surface tension recommended in the release is used also in the revised release, that was published in 2014. But since then, there have been many changes. Many new measurements have been published, also in the supercooled water region. A new temperature scale has appeared (ITS-90). That is why we have created a new correlation for the temperature dependence of surface tension of water. Our correlation is based on the theory of a critical point. We analyzed all existing experimental data, including the new experiments from the supercooled water region.

INTRODUCTION

In this paper we will focus on the temperature dependence of the surface tension of water. We will start with an overview of different forms of equations used for the temperature dependence of the surface tension.

The van der Waals equation [1, 2] for the temperature dependence of surface tension, which exactly fulfills the general conditions at the critical point, was published in 1894. The equation can be written in the form

$$\sigma \sim (T_c - T)^{3/2}, \quad (1)$$

where σ is the surface tension, T_c is the critical temperature, T is the temperature (in K). If we introduce a dimensionless variable $\tau = 1 - \frac{T}{T_c}$, the equation (Eq. 1) can be written in the form

$$\sigma \sim \tau^{3/2}. \quad (2)$$

Fergusson [3] generalized the equation (Eq. 2) and used the equation in the form

$$\sigma = \sigma_0 \tau^\mu. \quad (3)$$

He used the equation for 42 substances (excluding water) and he published the parameters σ_0 and μ for the substances. He found that the value of the exponent μ varies from 1.150 to 1.356. In another paper [4], Fergusson published the parameters σ_0 and μ for 14 substances and he got the mean value of $\mu = 1.21$.

Guggenheim [5] used the corresponding-states principle to correlate the surface tension and estimate the value of the exponent $\mu = 11/9$, which is about 1.222. Brock and Bird [6] used the same principle in their concept of the temperature dependence of the surface tension for non-polar liquids, and proposed a formula with the same exponent $\mu = 11/9$. Their formulas are applicable to temperatures far from the critical point. Widow and Fisk [7, 8] state that near the critical point

$$\sigma \sim \tau^\mu, \quad (4)$$

where the exponent μ belongs to so called critical exponents and can be calculated based on the methods of a modern theory of critical phenomena. Between the critical exponents the following correlation is valid:

$$\mu + \nu = \gamma + 2\beta, \quad (5)$$

and Widow and Fisk estimated (from the known values of the other critical exponents) that μ lies in the interval (1.22, 1.33). The most probable value was estimated to be 1.28 or 1.29.

There were attempts to create an equation for surface tension of water valid from the triple point up to the critical point. Grigull and Bach [9] developed a new empirical correlation

$$\sigma = \frac{a_1(T_c - T)^2}{1 + \beta(T_c - T)} + \sum_{n=2}^{n=5} a_n (T_c - T)^n. \quad (6)$$

The values of parameters are published in [9].

A similar equation was published by Vargaftik et al. in 1968 [10,11]:

$$\sigma = \sum_{n=1}^{n=9} a_n (T_c - T)^n. \quad (7)$$

The Eighth International Conference on the Properties of Water and Steam adopted a resolution to compile International tables of the surface tension of water. Three drafts of the tables were considered – tables submitted by a Japanese delegation, tables presented by a USSR delegation, and tables put forward by delegates of West Germany. Since the recommended values of surface tension of water in the data sets differed, it was decided to use the arithmetic means of the values. The table was adopted by the IAPS (International Association for the Properties of Steam) and it was promulgated in an official release in 1976 [12, 13].

Straub et al. [14] tested the following form of the equation for the temperature dependence of the surface tension of water:

$$\sigma = B\tau^\mu(1 + b\tau), \quad (8)$$

where $B=238.240214419$ mN/m, $b = -0.633572399671$, and $\mu = 1.62$. This equation uses $T_c = 647.3$ K. Straub et al. also tested a more general form:

$$\sigma = B\tau^\mu(1 + b\tau^{\mu_2}). \quad (9)$$

Straub et al. fit the equation to experimental data and they got $\mu = 1.288$ and $\mu_2 = 0.82$. This approximation was only slightly better than the equation (Eq. 8), and that is the reason, why the authors preferred the equation in the form (Eq. 8). Rathjen and Straub [15] published another version of the equation (Eq. 9), with constants $\mu = 1.272$ and $\mu_2 = 0.92$.

The IAPS [16] used the form and adopted the equation for describing the recommended values of:

$$\sigma = B\tau^\mu(1 + b\tau), \quad (10)$$

where $B=235.8$ mN/m, $b = -0.625$, and $\mu = 1.256$. This equation uses $T_c = 647.15$ K. This release is still valid, although the temperature of the critical point slightly changed, by ITS 90 $T_c = 647.096$ K [16].

Somayajulu [17] created two possible models

$$\sigma = a\tau^{\frac{5}{4}} + b\tau^{\frac{9}{4}}, \quad (11)$$

$$\sigma = a\tau^{\frac{5}{4}} + b\tau^{\frac{9}{4}} + c\tau^{\frac{13}{4}}. \quad (12)$$

The first term corresponds to the van der Waals correlation (Eq. 3), with an exponent $\mu = 1.25$. Somayajulu calculated the values of the three needed parameters for 64 fluids, including water. Somayajulu's results indicate that a three-constant equation (Eq. 12) fits the data much better than a two-constant equation (Eq. 11).

New expressions used for representing the surface tension data are based on the description of the critical behavior of fluids and on the corresponding-states principle. Based on the theory of the critical point, the surface tension approaching the critical point is described by Widom's scaling law [7]

$$\sigma = \sigma_0 \tau^\mu, \quad (13)$$

where σ_0 is the substance-dependent parameter and μ is the critical exponent, $\mu = 1.26$. For the description of many substances (including water) the equation (Eq. 13) is valid only in some vicinity of the critical point and corrections are needed. It is possible to use the so called Wegner's correction, expansion in powers τ^Δ , where $\Delta \approx 0.5$ is the correction to the scaling exponent [18, 19]. Schmidt et al. [20] suggest the following equation:

$$\sigma = \sigma_0 \tau^\mu (1 + \sigma_1 \tau^{0.5} + \sigma_2 \tau). \quad (14)$$

The equation was applied to refrigerants.

Mulero et al. [21] used surface tension data of 82 fluids and tested the model

$$\sigma = \sum_{i=0}^{k-1} \sigma_i \tau^{n_i}. \quad (15)$$

For water 797 data points were used. The temperature range of the data was from 233.22 K to 646.15 K, temperature of the critical point is 647.096 K. If we use the coefficient of equation (Eq. 15) for water from [21], we get for the surface tension of water

$$\sigma = 215.1 \tau^{1.233} (1 - 0.60716 \tau^{1.238}). \quad (16)$$

Many other papers tried to use the critical point concept in combination with the corresponding-states principle [22 – 26]. They very often use the correlations in the form of equation (Eq. 17). An interesting form for the surface tension was used in [24]. The form can be rewritten as:

$$\sigma = \sigma_0 \tau^\mu e^{-b\tau}. \quad (17)$$

Pátek et al. [27] revised a large set of experimental data (1620 data points) and developed a new correlation in the form of equation (Eq. 8), namely

$$\sigma = 233.58 \tau^{1.2527} (1 - 0.615946\tau). \quad (18)$$

NEW EQUATION

We think it is necessary to revise the current IAPWS standard (10). The reasons are as follows:

- The IAPWS standard has been valid since 1975.
- A new temperature scale was introduced.
- The value of the critical temperature, used for calculation of dimensionless variable τ , changed with a new temperature scale.
- New measurements for surface tension, especially in the area of supercooled water, appeared.

Pátek et al. [27] picked up 1620 data points that are available in literature in 211 data sets [27]. Their correlation is very good, but we have decided to develop a new correlation, based on the following rules:

- For the new correlation we must be careful when using “relative measurements”. Many of the measurements use some reference value that is used for calibration of the experimental device. For example, the surface tension of water at a reference temperature is very often used for calculation of the capillary diameter by capillary-rise method. As an example of the relative measurements it is possible to use recent measurements in supercooled water [28 – 30]. The measurements use the reference values gained from IAPWS and if we use the values, we get the IAPWS values again, mainly around the reference temperatures. We suggest to use independent reference values in case they are gained directly from measurements at reference temperatures [31].
- Pátek et al. [27] used the form (Eq. 10) for the correlation of experimental data, and fitted the coefficients B, b, μ . We suppose that μ is a critical exponent and it should not be fitted. Very often, the value 1.26 is used for the critical exponent μ . Hasenbusch estimates [32] that $\mu = 1.26004(20)$. We will use the value $\mu = 1.26$.
- We have used the data collected by Pátek et al. [27], and we have included some new data sets, for example the last measurements in supercooled water [30].
- We have recalculated all temperatures in experimental data points into ITS 90.
- We have excluded the data where the purity of the sample was not stated.
- We have calculated the correlation of surface tension in the form (Eq. 14) and we have excluded outliers. If the difference between a measured value of the surface tension and a calculated value from the correlation was greater than 1 mN/m (in absolute value), we have excluded all data from the data set from our data points.
- We set the weights of measurements that were measured before the 1920 to 0.5.

We started with 2001 data points in 252 data sets. After the reduction of experimental data points we have used 835 data points in 92 data sets.

We have tested two different models of the temperature dependence of the surface tension of water: the IAPWS form (Eq. 10) and the Wegner’s correction, expansion in powers τ^Δ (Eq. 14). The form (Eq. 10) was used in the IAPWS release, and the form also was used by Pátek et al. [27]. In both forms (Eqs. 10, 14) we fixed the exponent $\mu = 1.26$.

It means, we have calculated only two constants in the model (Eq. 10). We got the equation

$$\sigma = 236.625 \tau^{1.26} (1 - 0.625263\tau). \quad (19)$$

When we used the form (Eq. 14) to fit our data, we got the equation

$$\sigma = 241.322 \tau^{1.26} (1 - 0.0589 \tau^{0.5} - 0.56917 \tau). \quad (20)$$

For calculation of the correlation coefficients (Eqs. 19, 20) we have used the method of least squares and the procedure *nlinfit* from the MATLAB Statistics Toolbox.

In the model we need to fit three constants. To decide which model is better, we graphed the comparisons of the equations (Eqs. 19, 20) with IAPWS and Pátek et al. correlations. The result in the part of the supercooled region can be seen in Figure 1.

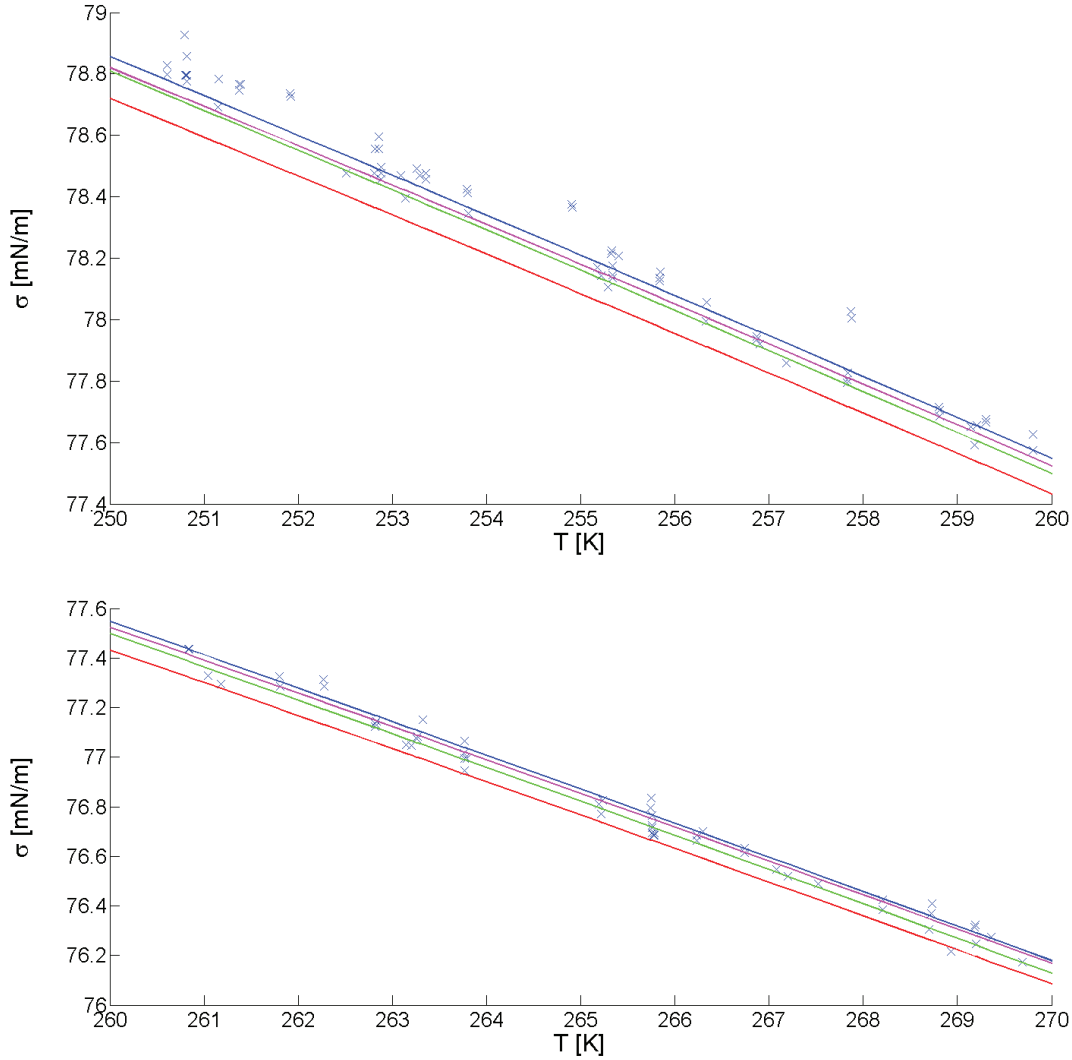


Figure 1. The surface tension in supercooled water. Blue crosses – experimental values, red line – IAPWS equation, green line – Pátek et al. equation, magenta line (Eq. 19), blue line (Eq. 20).

We can see that more parameters in the equation (Eq. 20) give a better result in the supercooled water region. The values of the Pátek et al. equation are lower because the data in the supercooled water region are relative and we used higher reference values to recalculate the data. A small systematic offset of the experimental data from our new equation can be detected for temperatures below -20 °C.

The differences between the experimental data points and the new equation (Eq. 20) and the IAPWS equation (Eq. 10) can be seen in Figure 2.

Uncertainties of the IAPWS equation (Eq. 10) were given in a table [16]. An estimated uncertainty of the surface tension in the table is 0.38 mN/m at 0 °C. It decreases to 0.1 mN/m at 370 °C. To determine the uncertainties of Eq. 20 we calculated standard deviations from experimental data at 10 °C intervals (to 100 °C) and at 30 °C intervals (over

100 °C). The results are displayed in Table 1 (here centers of temperatures intervals are given). One can see that the largest deviation is in the interval 90 °C - 100 °C. The new equation (Eq. 20) uncertainties are half in the comparison with those from IAPWS equation (Eq. 10) at the intervals below 80 °C. Above 100 °C, the deviations are almost the same. The reason of this is that basic measurements above 100 °C are the same for both equations [12].

TABLE 1. Uncertainties (Eq. 20)

t [°C]	-26	-15	-5	5	15	25	35	45	55	65
u(mN/m)	0.09	0.09	0.09	0.11	0.16	0.16	0.16	0.16	0.16	0.16
t [°C]	75	85	95	115	140	165	195	235	255	285
u(mN/m)	0.16	0.19	0.21	0.18	0.16	0.15	0.15	0.16	0.16	0.16
t [°C]	315	345	370							
u(mN/m)	0.14	0.1	0.06							

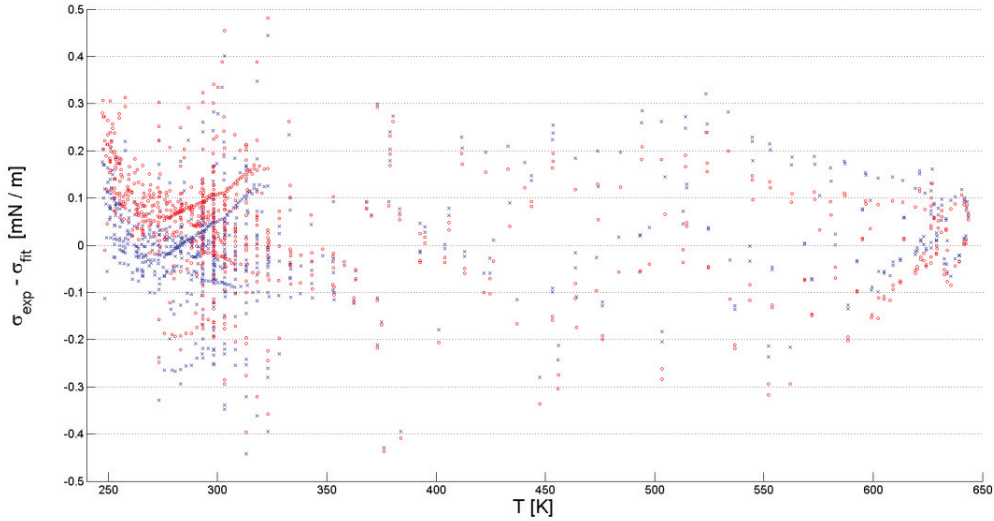


Figure 2. The differences between the experimental data points and the new equation (Eq. 20) (blue crosses), and the differences between the experimental data points and the IAPWS equation (Eq. 10) (red circles).

CONCLUSIONS

We presented reasons, why the IAPWS correlation for the surface tension of water needs to be revised. We reviewed existing forms of correlations and selected a form with a fixed first exponent. We suppose that the first exponent must be equal to the coefficient calculated from the theory of the critical point. We explored a large quantity of existing experimental points and we eliminated the experimental values that did not meet our requirements. We have found that for the description in the supercooled water region three constants are needed. We selected the form with Wegner's corrections.

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